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(54) Title: MODIFICATION OF ZEOLITES

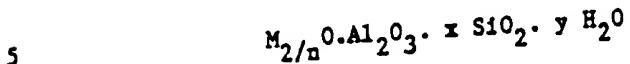
## (57) Abstract

A method for the modification of the framework structure of a zeolite comprises treating the zeolite with a solution in an organic solvent of a compound of an element capable of structural replacement of aluminium in the framework, the aluminium-replacing element being selected from, for example, boron, tin, silicon, titanium, germanium, gallium, phosphorus, beryllium and magnesium preferably in the form of their halides or organometallic compounds. Typical compounds are  $BCl_3$ ,  $BBr_3$ ,  $SnCl_4$ ,  $SnBr_4$ ,  $SnI_4$ ,  $SiCl_4$ ,  $SiI_4$ ,  $TiCl_4$ ,  $GeCl_4$ ,  $GaCl_4$ ,  $PCl_5$ ,  $BeCl_2$ ,  $MgCl_2$  and beryllium diphenyl. In a preferred embodiment the zeolite is reacted with silicon tetrachloride in carbon tetrachloride under reflux. However, the reaction time can be reduced by utilizing a solvent which has a molecular size which prevents it entering the channels of the zeolite, one such solvent being tetraethoxysilane.

Modification of Zeolites

This invention relates to a process for the chemical modification of zeolite structures.

Zeolites are crystalline hydrated aluminium silicates which have the general chemical formula:



where M is a cation of valency n and x is greater than or equal to 2.0. Structurally they have a porous framework based on an extended three-dimensional framework of  $SiO_4$  and  $AlO_4$  tetrahedra linked together through common oxygen atoms.

10 A large number of natural and synthetic zeolites are known but only a comparative few of these have found application as catalysts in the chemical industry. However, the important catalysts faujasite (in the form of the synthetic-zeolites X and Y), mordenite and ZSM-5 (Trade Mark) are used in substantial quantity: for example, more than 100,000 tons per year in 1970 were consumed in petroleum cracking. It is synthetic faujasite (as zeolite Y) which is principally used for this purpose.

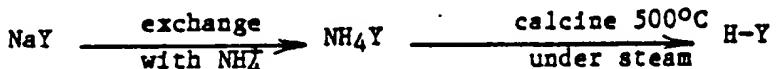
15 However, as synthesised, the value of x in the above formula for zeolite Y is approximately 5.0 and the resulting framework is not sufficiently stable to withstand the high temperatures ( $800^{\circ}C$ ) involved in the regenerator unit of cracking plants where coke is burnt off. (By "coke" is meant the deposits of carbon and low hydrogen content hydrocarbons that build up in petroleum cracking). To improve the thermal stability of the zeolite, the  $SiO_2/Al_2O_3$  ratio has to be increased.

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Several methods have been proposed but, principally for reasons of cost, the preferred methods are based on the following chemical process:



5 that is, the hydrogen ( $\text{H}^+$ ) form is made by calcination of the ammonium ( $\text{NH}_4^+$ ) exchanged form in the presence of steam at high temperatures. This results in some of the aluminium atoms leaving the framework and being deposited in the channel network as extra-framework aluminium. The vacancies are filled by atoms 10 of silicon diffusing from other parts of the crystallites. Obviously the net result is the production of a partially crystalline material along with some amorphous material and the introduction of some mesopores into the system. The resulting material, however, is an excellent selective catalyst.

15 The other methods which can be used to increase the silicon to aluminium ratio are (a) extraction of aluminium by EDTA (ethylenediaminetetraacetic acid) (b) acid treatment and (c) use of silicon tetrachloride vapour. EP-A-82211 describes the use of an aqueous solution of a fluorosilicate to replace aluminium with 20 silicon in the framework. The use of the  $\text{SiCl}_4$  vapour, as described for example in EP-A-62123 and EP-A-72397, has some useful effects. The vacancies in the framework, produced by the extraction of aluminium, are healed by silicon atoms from the tetrachloride, and, the aluminium removed from the framework is 25 converted to its volatile trichloride effecting removal from the system. However, problems associated with the vapour phase process are (a) the cost of the silicon tetrachloride, (b) the high temperature required, and, (c) the potential danger of collapse of the structure of the framework unless the temperature 30 is strictly controlled.

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EP-A-210018 describes another process for the modification of zeolite framework structures which involves treatment of the zeolite with a molten salt medium which contains a reactive component which has a "radius ratio" of less than 0.6, the "radius ratio" being defined as the ratio of the crystal ionic radius of the central atom of the reactive component to that of the oxygen anion  $O^{2-}$ . The method is applicable to porous crystalline minerals which have pores large enough to sorb normal hexane. Examples of the components which have the required radius ratio are: the trichlorides of aluminium, boron, iron, phosphorus and gallium, and the tetrachlorides of titanium and tin, the  $Si^{4+}$  ion being also mentioned. The method may be used to insert aluminium into high silicon zeolite frameworks or otherwise alter the framework without substantial alteration of its structure.

An object of the present invention is to provide an improved method for the modification of zeolite framework structures.

According to the present invention there is provided a method for the modification of the framework structure of a zeolite comprising treating the zeolite with a solution in an organic solvent of a compound of an element capable of structural replacement of aluminium in the framework.

The compound is preferably a metal halide of the aluminium-replacing element, examples being:  $BCl_3$ ,  $BBr_3$ ,  $SnCl_4$ ,  $SnBr_4$ ,  $SnI_4$ ,  $SiCl_4$ ,  $SiI_4$ ,  $TiCl_4$ ,  $GeCl_4$ ,  $GaCl_4$ ,  $PCl_5$ ,  $BeCl_2$ ,  $AlCl_3$  and  $MgCl_2$ . However, organometallic compounds of the selected element may also be suitable, for example, beryllium diphenyl.

The zeolite may be, for example, Erionite, Beta, ZSM-5, ZSM-11 (Trade Marks), Mordenite, Chabazite, and Offretite.

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The selection of the solvent is not critical. Solvents, and solvent mixtures, of small molecular size, such as carbon tetrachloride and ethanol, are suitable but the reaction may be accelerated by the use of a solvent of a molecular size which is 5 too large to enter the channels of the zeolite, one particularly preferred solvent for this purpose being tetraethoxysilane  $[(C_2H_5O)_4Si]$ .

The temperature of the treatment is not of critical 10 importance but would normally be carried out at the reflux temperature of the solvent in order to minimise the treatment time.

The method of the invention may include a pretreatment step in which the zeolite is treated with acid to effect a desired degree of dealumination, prior to treatment with the solvent solution compound of the aluminium-replacing element. Since the 15 degree of dealumination with acid is restricted only by the need to maintain the integrity of the zeolitic structure, the use of the acid pretreatment step enables the production of zeolites with very high silicon to aluminium ratios.

As well as increasing the thermal stability of the zeolite 20 increase of the silicon to aluminium ratio improves the Bronsted acidity of the OH groups which remain in the dealuminated framework.

The invention will now be described, by way of illustration, in the following Examples.

25 EXAMPLE 1

About 1 gram of NaY zeolite was calcined in a muffle furnace at  $600^{\circ}C$  for a few hours. The zeolite was then cooled to 30  $80-100^{\circ}C$  in a desiccator and 25ml of carbon tetrachloride ( $CCl_4$ ) was then added with continuous stirring to form a slurry. Various amounts (0.10 to 0.77ml) of silicon

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5 tetrachloride ( $SiCl_4$ ) were added to several separate samples of the slurry which were then refluxed at a fixed temperature (58-59°C; 76-77°C) for a period of three hours. The final slurry was then centrifuged to separate the solid and liquid phases. Three successive portions of  $CCl_4$  (approximately 15ml) followed by three successive portions of ethanol (approximately 15ml) were employed during the solid/liquid separation stage. The product was dried on a water bath and treated with sodium chloride solution (1-5M) repeatedly to convert the zeolite to the pure sodium form. The product was then well washed with distilled deionised water (boiled and cooled out of contact with air) until free of chloride, dried at 100°C and calcined at 10

10 600°C for one hour.

15 The calcined zeolite was allowed to cool and treated with sodium chloride solution (1-5M at pH 8-9) repeatedly. The final product was well washed until chloride-free, filtered and dried at 100°C.

20 Analysis of the dealuminated samples was as follows:

(a) Dealuminated samples were calcined at 600°C to obtain the dry weight and the residues dissolved to determine the aluminium content by EDTA titration.

(b) Sodium was determined by  $^{22}Na$  tracer method.

(c) Silicon was estimated by difference.

(d) Collapse temperature was determined by differential thermal analysis using a Du Pont 990 Thermal Analyser (in nitrogen).

25

The results are reported in Table I below.

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TABLE I

	Sample No.	SiCl <sub>4</sub> added(ml)	Reflux T°C	Al mmol/g	Na mmol/g	Al /u.c.*	Collapse T°C
5	CS0.10/58	0.10	58-59	2.95	2.92	49.3	1012
	CS0.20/58	0.20	58-59	2.97	2.89	50.1	1014
	CS0.33/58	0.33	58-59	2.79	2.83	46.8	1023
	CS0.40/58	0.40	58-59	2.84	2.86	47.5	1015
	CS0.77/58	0.77	58-59	2.86	2.82	47.3	993
10	CS0.10/76	0.10	76-77	2.98	2.94	49.5	984
	CS0.27/76	0.27	76-77	2.78	2.72	45.8	1009
	CS0.33/76	0.33	76-77	2.71	2.61	45.3	1021
	CS0.77/76	0.77	76-77	2.74	2.64	44.8	1007
Starting Material, NaY				3.28	3.11	56.1	933

\* based on total Al present - 192 Al sites in unit cell (u.c.)

15 EXAMPLE 2

The same procedure as described in Example 1 was used except that 15ml of CCl<sub>4</sub> and 0.3ml SiCl<sub>4</sub> were refluxed with NaY zeolite with different water content at 59°C for 20 minutes. The results are given in Table II below.

20

TABLE II

	Sample No.	Water content/u.c.	Al mmol/g	Na mmol/g	Al /u.c.	Collapse T°C
25	CS (1)	11	2.96	2.89	49.9	1002
	CS (2)	30	2.90	2.91	48.4	1015
	CS (3)	23	2.90	2.89	48.7	1013
	CS (4)	39	2.90	3.01	48.1	1008
	0.3 CSH	245	2.47	2.38	39.8	998

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EXAMPLE 3

Using the procedure described in Example 1 above, 20ml of  $\text{CCl}_4$  and 10ml  $\text{SiCl}_4$  were refluxed with zeolites with different cationic forms at  $58-60^\circ\text{C}$  for one hour.

5 The results are given in Table III below.

TABLE III

Sample No.	Cationic form	Al mmol/g cation	Na/other mmol/g	Al mmol/g /u.c.	Collapse $T^\circ\text{C}$
10	$\text{Li}_Y$ 600*	3.01	2.66	49.0	1001
	$\text{Na}_Y$ 600	2.70	2.64	44.5	1030
	$\text{K}_Y$ 600	2.89	2.71	47.1	1015
	$\text{Cs}_Y$ 600	3.12	3.11	52.4	996
	$\text{Ba}_Y$ 600	3.09	2.32	50.0	982
	$2\text{La}_Y$ 600	2.84	1.71/0.66	52.0	956
15	$\text{Ce}_Y$ 600	2.91	1.77/0.69	53.7	978

\* zeolite  $Y$  calcined at  $600^\circ\text{C}$

\*\*  $16\text{ Na}^+$  in small cages.

EXAMPLE 4

Using the same procedure as is described in Example 1, 30ml of  $\text{SiCl}_4$  was refluxed with  $\text{Na}_Y$  zeolite at  $57^\circ\text{C}$  and samples 20 were withdrawn after 30, 60 and 90 minutes.

The results are reported in Table IV below.

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TABLE IV

	Sample No.	Reflux Time (min)	Al mmol/g	Na mmol/g	Al /u.c.	Collapse T°C
5	S0.50/57	30	2.31	2.24	37.5	1031
	S1.0/57	60	2.33	2.20	37.0	-
	S1.5/57	90	2.32	2.25	37.3	1041
	SS0.5/1.5	30	2.16	1.93	33.2	1070

Samples S0.50/57, S1.0/57 and S1.5/57 were mixed with 15ml SiCl<sub>4</sub> and refluxed at 57°C for 30 minutes to produce sample SS0.5/1.5.

10 EXAMPLE 5

Using the procedure described in Example 1, 15ml of SiCl<sub>4</sub> were refluxed with zeolite produced from Example 1 (Sample Nos. CS0.10/58 + CS0.20/58 + CS0.10/76) at 57°C for 30 minutes. Four cycles were carried out.

15 The results are given in Table V below.

TABLE V

	Sample No.	Reflux Cycle	Al mmol/g	Na mmol/g	Al /u.c.	Collapse T°C
20	S	1	2.09	2.04	33.4	1056
	SS	2	2.00	1.81	30.6	1063
	SSS	3	1.83	1.66	27.8	1078
	SSSS	4	1.81	1.62	27.4	1073
	Starting material dealuminated zeolite					49.6

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Table VI reports the results of infra-red characterisation studies and Table VII the results of X-ray diffraction studies, confirming the increase of the Si/Al ratio of the zeolite Y framework.

TABLE VI

5	Sample	Al/u.c.	Asymmetric (cm <sup>-1</sup> )	Symmetric (cm <sup>-1</sup> )	Double Rings (cm <sup>-1</sup> )
	No.				
	NaY	56.1	1015 s	790 m	582 m
	CS (1)	50.1	1023 s	793 m	584 m
10	CS (4)	48.1	1030 s	793 m	585 m
	CS0.33/58	46.8	1030 s	798 m	588 m
	CS0.33/76	45.3	1030 s	800 m	588 m
	S	33.4	1042 s	805 m	593 m
	SS	30.6	1045 s	810 m	597 m
15	SSSS	27.4	1050 s	810 m	597 m

s = strong

m = medium

TABLE VII

20	Sample	Lattice Constant $a_0 + 0.06 \text{ \AA}$	Al/u.c.
	No.		
	NaY	24.59	56.1
	SO.50/57	24.68	37.5
	S1.0/57	24.48	37.0
	S1.5/57	24.48	37.3
25	SS0.5/1.5	24.41	33.2
	S	24.41	33.4
	SS	24.41	30.6
	SSS	24.38	27.8
	SSSS	24.38	27.4
30	CS0.33/57	24.53	46.8
	CS0.77/57	24.53	47.3

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EXAMPLE 6

Table VIII below reports the products (in sodium form) resulting from the dealumination of sodium Y zeolites by  $\text{SiCl}_4$  in the solvent tetraethoxysilane  $[(\text{C}_2\text{H}_5\text{O})_4\text{Si}]$  (TES). The 5 methods used were as follows:

Method A (Sample STES NaY)

About 1 gram of sodium Y zeolite [ZY(H)] was calcined at 600°C and allowed to cool in a desiccator. 25ml of TES were added to the zeolite followed by 1ml of  $\text{SiCl}_4$ . The mixture was 10 refluxed for one hour.

Method B (Sample STES DY)

The method was as described under Method A above but sodium Y zeolite [ZY(D)] was used.

Method C (Samples STES DY 0.5; STES DY1; STES DY2 and STES DY18B)

15 About 19 grams of sodium Y zeolite (ZY[D]) was calcined at 600°C and allowed to cool in a desiccator. 45 ml of  $\text{SiCl}_4$  were added to the zeolite with constant stirring for 1-2 minutes followed by 70ml of TES. The resultant slurry was refluxed for 18 hours. Zeolite slurry samples were withdrawn after 30 minutes, 20 one hour, two hour and 18 hour intervals.

From the results reported in Table VIII below, particularly the results of Method C, it can be seen that dealumination is substantially complete within the first 30 minutes of reaction time. These samples all showed very good crystallinity; as good 25 as the starting sodium Y zeolite.

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TABLE VIII

Sample No.	Reflux T°C	H <sub>2</sub> O %	Al mmol/g	<sup>22</sup> Na mmol/g	Si/Al ratio
1	1STES Na <sub>Y</sub>	110-116	22.76	3.02	2.87
5	1STES DY	103	22.92	3.02	2.88
	STES DY 0.5	80	21.15	2.28	4.43
	STES DY 1	78	21.28	2.28	4.41
	STES DY 2	78	20.89	2.46	4.05
	STES DY 18B	78	21.32	2.28	4.41

TABLE VIII (continued)

Sample No.	Al/u.c. T°C	Collapse	Lattice Constant Å
1	1STES Na <sub>Y</sub> 49.6	991	-
10	1STES DY 49.5	999	-
15	STES DY 0.5 35.4	1052	24.34
	STES DY 1 35.5	1052	24.36
	STES DY 2 38.0	1050	-
	STES DY 18B 35.5	1010	24.36

EXAMPLE 7

20 Table IX reports the product (in sodium form) resulting from the dealumination of sodium Y zeolite by a SiCl<sub>4</sub>/CCl<sub>4</sub>/C<sub>2</sub>H<sub>5</sub>OH solvent mixture.

25 About one gram of sodium Y zeolite [56Al/u.c., Z<sub>Y</sub>(H)] was calcined at 600°C for a few hours and allowed to cool in a desiccator. 12.5ml of CCl<sub>4</sub> were added to the zeolite followed by 1ml of SiCl<sub>4</sub>. The mixture was refluxed at 56°C for 30

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minutes when 12.5ml of ethanol were introduced. Refluxing at 63°C was continued for a further 30 minutes.

TABLE IX

	Sample No.	1 CSEt <sub>2</sub> NaY
5	Reflux	56/63°C
	H <sub>2</sub> O	22.12%
	Al	2.9 mmol/g
	<sup>22</sup> Na	2.97 mmol/g
	Si/Al ratio	3.04
10	Al/u.c.	47.5
	Collapse	994°C

EXAMPLE 8

Table X below reports the products (in sodium form) resulting from the dealumination of sodium Y zeolites by 15 SiCl<sub>4</sub>/ethanol solutions.

TABLE X

Sample No.	Reflux T°C	H <sub>2</sub> O %	Al mmol/g	<sup>22</sup> Na mmol/g	Si/Al ratio
20	SEtDY 0.5	70	22.41	2.72	3.39
	SEtDY 1	70	22.46	2.71	3.40
	SO.5EtDY 0.5	70	22.21	2.60	3.62
	SO.5EtDY 1	70	22.47	2.62	3.58
	5SEtDY	78.9	21.73	2.76	3.35
	10SEt10EtDY	78.3	22.09	2.81	3.25
25	1CSEt5NaY	75.2	22.34	2.79	3.29
	SEtNaY	57/74	19.79	2.81	3.39
	1SEtNaY	57/74	23.24	2.88	3.07
	SEtG	57/74	21.31	2.65	3.60

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TABLE X (continued)

Sample No.	Al/u.c.	Collapse $\tau^{\circ}\text{C}$
5	SEtDY 0.5	43.7
	SEtDY 1	43.6
	SO.5EtDY 0.5	41.6
	SO.5EtDY 1	41.9
10	555EtDY	44.1
	10S10EtDY	45.2
	1CSEt5NaY	44.8
	SEtNaY	43.7
	1SEtNaY	47.2
	SEtG	41.7
		1014
		1019
		1027
		1028
		1017
		1007
		1006
		990
		1001
		1030

EXAMPLE 915      Method (i) (Samples SEtDY 0.5 and SEtDY 1)

About 5 grams of the sodium form Y zeolite (approximately 56 Al/u.c.; ZY[D]) was calcined at 600°C for a few hours and allowed to cool in a desiccator. 20 ml of  $\text{SiCl}_4$  were added to the zeolite and stirred for 5 minutes. Five successive portions of  $\text{CCl}_4$  of approximately 20ml were added to the zeolite slurry and the  $\text{CCl}_4$  was discarded after centrifuging the slurry. 80ml of ethanol were then added and refluxed for one hour. Approximately 50ml of the slurry was withdrawn after 30 minutes and the rest after one hour.

25      Method (ii) (Samples SO.5EtDY0.5 and SO.5EtDY 1)

The method was the same as Method (i) above except that the

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contact time of the zeolite and  $\text{SiCl}_4$  was increased to 15 minutes.

Method (iii) (Sample 5S5EtDY)

5 About 5 grams of sodium Y zeolite ( $\text{ZY}[\text{D}]$ ) was calcined at  $600^{\circ}\text{C}$  for a few hours and cooled in a desiccator. 5ml of  $\text{SiCl}_4$  were added to the zeolite and stirred for 5 minutes. 50ml of ethanol were then added to the slurry and refluxed for one hour.

Method (iv) (Sample 10S10EtDY)

10 The method was the same as Method (iii) above except that 10ml of  $\text{SiCl}_4$  were used and the  $\text{SiCl}_4$ -zeolite contact time was increased to 10 minutes.

Method (v) (Sample 1CSEt5NaY)

15 About one gram of sodium Y zeolite ( $\text{ZY}[\text{H}]$ ) was calcined at  $600^{\circ}\text{C}$  for a few hours and allowed to cool in a desiccator. About 1ml of  $\text{SiCl}_4$  was added to the zeolite and stirred for 5 minutes. 25ml of ethanol were then added to the slurry and refluxed for one hour.

Method (vi) (Sample SEtNaY)

20 About one gram of sodium Y zeolite ( $\text{ZY}[\text{H}]$ ) was calcined at  $600^{\circ}\text{C}$  for a few hours and allowed to cool in a desiccator. About 15ml of  $\text{SiCl}_4$  were added to the zeolite and refluxed for 30 minutes. The zeolite slurry was then centrifuged to separate the solid and liquid phases. The zeolite was washed with three successive 10ml portions of  $\text{CCl}_4$ . About 25ml of ethanol were added to the zeolite and refluxed for 15 minutes.

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Method (vii) (Sample 1SEtNaY)

The method was the same as Method (vi) except that 1ml of SiCl<sub>4</sub> and 14ml of CCl<sub>4</sub> were used in the first reflux.

Method (viii) (Sample SEtG)

5 The method was the same as Method (vi) except that 10 grams of sodium Y zeolite (ZY[G]), 80ml of SiCl<sub>4</sub> and 100ml of ethanol were used.

EXAMPLE 10

10 Table XI below reports the products resulting from the dealumination of sodium Y zeolites followed by treatment with various mixtures including SiCl<sub>4</sub> as a component.

TABLE XI

Sample No.	Temperature °C	H <sub>2</sub> O %	Al mmol/g	<sup>22</sup> Na mmol/g	Si/Al ratio
<u>Method I - CSH SERIES</u>					
15 CS4	100	59	24.30	2.90	2.97
CSH48	100	59	24.73	2.42	3.80
CSH40	100	59	24.74	2.21	4.31
CSH32	100	59	23.73	1.97	5.08
20 CSH24	100	59	24.96	1.56	6.64
CSH16	100	59	23.99	1.22	9.00
<u>Method II - HCS SERIES</u>					
HCS32	100	59	18.67	2.11	5.05
HCS16	100	59	17.52	1.25	9.61

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Method III - STES SERIES

	STES NaY	300	71	21.78	2.96	3.05	3.02
	STES H48	300	71	21.58	2.66	2.76	3.53
	STES H40	300	69	20.24	2.44	2.51	4.07
5	STES H32	120	69	16.64	2.19	2.21	4.97
	STES H24	120	67	17.27	1.74	1.88	6.52
	STES H16	120	69	16.05	1.38	1.45	8.74

TABLE XI (continued)

	Sample No.	Al/u.c.	Collapse T°C
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		<u>Method I - CSH SERIES</u>	
	CS4	48.4	1008
	CSH48	40.0	1021
	CSH40	36.2	1031
15	CSH32	31.6	1023
	CSH24	25.1	981
	CSH16	19.2	990

		<u>Method II - HCS SERIES</u>	
	HCS32	31.7	1021
20	HCS16	18.1	1014

		<u>Method III - STES SERIES</u>	
	STES NaY	47.8	993
	STES H48	42.4	1001
	STES H40	37.9	1013
25	STES H32	32.2	991
	STES H24	25.5	949
	STES H16	19.7	931

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5 The dealuminated zeolite is made by treatment of sodium Y zeolite with hydrochloric acid. Dealumination does not occur when the pH of the acid is greater than 2.30, while complete dealumination occurs at pH less than 0.46. It appears that four hydrogen atoms are required to remove one aluminium atom. This acid dealumination results in a structure which is less crystalline than the initial zeolite (due to accumulated defects in the structure) and is not thermally stable. However, treatment with  $\text{SiCl}_4$ -containing mixtures allows insertion of 10 silicon into the zeolite matrix and gives a product of reasonable thermal stability.

The treatment with  $\text{SiCl}_4$  was by three different methods.

Method I - CSH SERIES

15 About 0.5 gram of dealuminated Y zeolite (by HCl treatment) in sodium form was dehydrated in an oven at  $100^\circ\text{C}$  for a few hours, and then allowed to cool in a desiccator. The zeolite was then mixed with 15ml of  $\text{CCl}_4$ , followed by 0.30ml of  $\text{SiCl}_4$  and refluxed for 30 minutes.

Method II - HCS SERIES

20 The procedure was the same as Method I above except that 10ml of  $\text{CCl}_4$  and 5ml of  $\text{SiCl}_4$  were used.

Method III - STES SERIES

25 About one gram of dealuminated Y zeolite (by HCl treatment) in sodium form (as used in Methods I and II above) was dehydrated in an oven at two temperatures ( $120^\circ\text{C}$  and  $300^\circ\text{C}$ ) for a few hours and then allowed to cool in a desiccator. The zeolite was

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then mixed with 3ml of  $\text{SiCl}_4$  with constant stirring for 5 minutes. 20ml of TES was added to the slurry and refluxed for one hour. The highly dealuminated samples (those with fewer than 32 atoms of aluminium per unit cell) had poor crystallinity.

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CLAIMS

1. A method for the modification of the framework structure of a zeolite, comprising treating the zeolite with a solution in an organic solvent of a compound of an element capable of structural replacement of aluminium in the framework.
2. A method as claimed in claim 1, in which the aluminium-replacing element is selected from boron, tin, silicon, titanium, germanium, gallium, phosphorus, beryllium aluminium and magnesium.
3. A method as claimed in claim 1 or claim 2, in which the said compound is selected from the halides of the aluminium-replacing element.
4. A method as claimed in claim 3, in which the halide is selected from  $BCl_3$ ,  $BBr_3$ ,  $SnCl_4$ ,  $SnBr_4$ ,  $SnI_4$ ,  $SiCl_4$ ,  $SiI_4$ ,  $TiCl_4$ ,  $GeCl_4$ ,  $GaCl_4$ ,  $PCl_5$ ,  $BeCl_2$ ,  $AlCl_3$  and  $MgCl_2$ .
5. A method as claimed in claim 4, in which the halide is silicon tetrachloride.
6. A method as claimed in claim 1 or claim 2, in which the said compound is an organometallic compound.

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7. A method as claimed in claim 6, in which the organometallic compound is beryllium diphenyl.
8. A method as claimed in any preceding claim, in which the organic solvent is carbon tetrachloride or ethanol or a mixture thereof.
9. A method as claimed in any of claims 1 to 7, in which the solvent is an organic liquid having molecules which are too large to enter the channels of the zeolite.
10. A method as claimed in claim 9, in which the solvent is tetraethoxysilane.
11. A method as claimed in any preceding claim, in which the zeolite is selected from Erionite, Beta, ZSM-5, ZSM-11, Mordenite, Chabazite, and Offretite.
12. A method as claimed in any preceding claim, in which the treatment carried out under solvent reflux conditions.
13. A method as claimed in any preceding claim, in which the zeolite is pretreated with acid to remove aluminium therefrom.
14. A method of thermally cracking petroleum hydrocarbons characterised in that said cracking is conducted in the presence of a modified zeolite; said zeolite being the product of a process as claimed in any of the preceding claims.

# INTERNATIONAL SEARCH REPORT

International Application No. PCT/GB 87/00591

## I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all)

According to International Patent Classification (IPC) or to both National Classification and IPC  
 IPC: 4 C 01 B 33/28; C 01 B 35/10; B 01 J 29/04; C 10 G 11/05

## II. FIELDS SEARCHED

Classification System	IPC <sup>4</sup>	Minimum Documentation Searched <sup>7</sup>	
		Classification Symbols	Classification Symbols
		B 01 J 29/00	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>8</sup>			

## III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup>

Category <sup>10</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
A	GB, A, 1332468 (UNION CARBIDE) 3 October 1973, see page 3, lines 99-130 --	
A	US, A, 3528768 (S. TUCKER) 15 September 1970 --	
A	EP, A, 0012570 (MOBIL OIL) 25 June 1980, see pages 17-22 --	
A	EP, A, 0037630 (MOBIL OIL) 14 October 1981, see pages 21-24 --	
A	EP, A, 0050907 (MOBIL OIL) 5 May 1982, see pages 14-15 --	
A	EP, A, 0040900 (MOBIL OIL) 2 December 1981, see pages 20-21 --	
A	EP, A, 0034918 (MOBIL OIL) 2 September 1981, see pages 20-21 -----	

\* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

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"P" document published prior to the international filing date but later than the priority date claimed

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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"Z" document member of the same patent family

## IV. CERTIFICATION

Date of the Actual Completion of the International Search

8th December 1987

Date of Mailing of this International Search Report

25 JAN 1988

International Searching Authority

EUROPEAN PATENT OFFICE

Signatures of Authorized Officer

P.C.G. VAN DER PUTTEN

ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO. **102000000000**

GB 8700591  
SA 18338

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 05/01/88. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
GB-A- 1332468	03-10-73	None		
US-A- 3528768	15-09-70	None		
EP-A- 0012570	25-06-80	CA-A- 1122228 US-A- 4371721 US-A- 4181811 JP-A- 55083716		20-04-82 01-02-83 01-01-80 24-06-80
EP-A- 0037630	14-10-81	US-A- 4278827 JP-A- 56145227 US-A- 4394300 CA-A- 1180307		14-07-81 11-11-81 19-07-83 01-01-85
EP-A- 0050907	05-05-82	US-A- 4302620 JP-A- 57082326 AU-A- 6761181 US-A- 4358397 CA-A- 1180313 AU-B- 544036		24-11-81 22-05-82 06-05-82 09-11-82 01-01-85 16-05-85
EP-A- 0040900	02-12-81	US-A- 4276437 JP-A- 57010337 AU-A- 6977181 CA-A- 1153746 AU-B- 544380		30-06-81 19-01-82 26-11-81 13-09-83 23-05-85
EP-A- 0034918	02-09-81	US-A- 4260843 JP-A- 56133030 CA-A- 1181056		07-04-81 17-10-81 15-01-85

